



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C02F 3/30	A1	(11) International Publication Number: WO 98/07664 (43) International Publication Date: 26 February 1998 (26.02.98)
<p>(21) International Application Number: PCT/NL97/00482</p> <p>(22) International Filing Date: 25 August 1997 (25.08.97)</p> <p>(30) Priority Data: 1003860 23 August 1996 (23.08.96) NL 1005343 21 February 1997 (21.02.97) NL</p> <p>(71) Applicant (for all designated States except US): TECHNISCHE UNIVERSITEIT DELFT [NL/NL]; Julianalaan 134, NL-2628 BL Delft (NL).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): VAN LOOSDRECHT, Marinus, Cornelis, Maria [NL/NL]; Viool 99, NL-2678 HL De Lier (NL). JETTEN, Michaël, Silvester, Maria [NL/NL]; Schijfflaan 12, NL-2625 KG Delft (NL).</p> <p>(74) Agent: ALTENBURG, Bernardus, Stephanus, Franciscus; Octrooibureau Los en Stigter B.V., Weteringschans 96, NL-1017 XS Amsterdam (NL).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report.</i> <i>In English translation (filed in Dutch).</i></p>
<p>(54) Title: METHOD OF TREATING AMMONIA-COMPRISING WASTE WATER</p>		
<p>(57) Abstract</p> <p>The invention relates to a method of treating ammonia-comprising waste water in which the bicarbonate ion is the counter ion of the ammonium ion present in the waste water. According to the invention half the ammonium is converted into nitrite, yielding an ammonia- and nitrite-containing solution, and in the second step the nitrite is used as oxidant for the ammonia. In the method according to the invention the conversion of half the ammonia into nitrite occurs automatically, providing a method which requires fewer controls. Also, the method according to the invention requires no external additive.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

Method of treating ammonia-comprising waste water

The present invention relates to a method of treating ammonia-comprising waste water, wherein in a first step ammonia-comprising waste water is subjected to a nitrification treatment by using a nitrifying microorganism and by the addition of oxygen, yielding a solution comprising an oxidation product of ammonia, and in a second step the oxidation product of ammonia together with ammonia is converted into nitrogen, through the influence of a denitrifying microorganism.

Such a method is known from US patent specification No. 5,078,884. The nitrate formed by the oxidation of ammonia is used as an oxidant to convert, under substantially anaerobic conditions and with the aid of a microorganism, still to be degraded ammonia which acts as electron donor. During this process nitrogen is formed which is discharged into the atmosphere.

The disadvantage of this method is that there is no reliable degradation of ammonia, as can be seen in (the right half of) Fig. 2 of said publication. This means that undesirable discharges into the surface water may take place. To prevent this, all kinds of investments such as control and measuring equipment would be required. Finally, this method involves the addition of lye (see reaction equation 5 of said publication), which must also be controlled.

The objective of the present invention is to improve the method according to the preamble and in particular to provide a cost-effective, more reliable method which requires no additives and partly because of that, is simpler from a control-technological point of view.

Surprisingly, this objective can be achieved by a method which is characterized in that by using bicarbonate-containing waste water which is substantially stripped of bicarbonate by the supply of air, and in the first step maintaining the pH at ≤ 7.2 by controlling the aeration, part of the ammonia present in the waste water is con-

verted into nitrite, yielding a nitrite-containing solution, and in the second step the denitrifying microorganism uses the thus formed nitrite as oxidant for the remaining ammonia.

5 In this manner a method is provided offering considerable advantages, one of which being a substantially more self-regulatory nature. Moreover, the use of additives is avoided.

From the prior art a method is known, comprising a
10 nitritification step in which ammonia is converted into nitrite. In a denitritification step the nitrite is converted into nitrogen while an organic carbon source is added as substrate for a denitritifying organism. As organic carbon source methanol is used. When said methanol
15 is degraded, acid, formed during the nitritification step, is consumed, providing the pH control of the denitritification process. The disadvantage of this non-continuous method is that an additive is required and much control is required such as time control and substrate feed control.
20 The total conversion of ammonia is not under all conditions satisfactory and is limited to at the most 90% and for this reason a subsequent treatment is often required.

A first favourable embodiment of the method is characterized in that in the first step the ammonia-containing
25 ing waste water is fed to a nitritification reactor in an amount such that the nitritification reactor operates without sludge retention, the temperature of a solution subjected to nitritification is maintained at between 25 and 60°C and the pH at between 6 and 7.2.

30 In this manner favourable conditions are provided for the conversion of ammonia to nitrite, not nitrate.

In the second step, the temperature of the solution in the denitritification reactor being subjected to the denitritification treatment is preferably maintained at
35 between 25 and 60°C and the pH at between 6 and 9.

In this manner favourable conditions are provided for the conversion of nitrite and ammonia into nitrogen.

According to a second embodiment of the method in accordance with the invention the first step and the sec-

ond step are carried out simultaneously in one bioreactor, in which bioreactor nitrifying and denitrifying microorganisms are present in a solid phase, the nitrifying microorganism being substantially present in the outer, aerobic part of the solid phase and the denitrifying microorganism being substantially present in the anaerobic inner part of the solid phase, and oxygen, dependent on the ammonia concentration in the bioreactor, is supplied in an amount limiting the first step.

10 The advantage of this method is that only one reactor is required. The preferably somewhat rough carrier comprises a biofilm, that is to say a layer comprising the nitrifying and denitrifying microorganisms, and the first step takes place in the outer, aerobic part of the bio-
15 film. Because of oxygen limitation this outer, aerobic part of the biofilm is unable to convert more than 50% of the ammonia supplied and the ammonia, together with the nitrite formed in the outer, aerobic part of the biofilm, will be converted in the inner, aerobic part of the bio-
20 film into nitrogen. The solid phase may consist of a spontaneously formed aggregate.

Preferably as solid phase a phase chosen from a biofilm-carrying particulate carrier and a biofilm-carrying immobile carrier is used.

25 If the carrier is particulate, the size of the carrier is preferably 0.1 to 1 mm. In this manner a high biomass density is provided and the size of the bioreactor can be kept to a limit. In a typical case the ammonia load of the biofilm surface is greater than 2-3 g N/m²·day.
30 Some roughness of the carrier surface is an advantage.

In the second step the temperature of a solution subjected to the denitrification-nitrification reaction in the reactor is preferably maintained at between 5 and 60°C and the pH at between 6 and 9.

35 This creates favourable conditions for the conversion of ammonia into nitrogen.

The invention will be further elucidated by means of the detailed specification hereinbelow referring to an

Example of the method according to the invention, the parameters of which are given in the accompanying Figure.

The method according to the present invention comprises a nitritification reaction and a denitritification
5 reaction. As can be seen from the overall-reaction equation I shown on the formula sheet, and as will be elucidated below, no addition of pH-adjusting means is necessary. The nitritification according to reaction equation II yields two equivalents of protons per converted equivalent
10 ammonia. In waste water that can be suitably treated by applying the invention, HCO_3^- is the counter ion of the ammonia ion. Examples of such waste water include the percolation water from rubbish dumps and the effluent from aerobic purifications. The supply of air necessary for the
15 oxidation of ammonia during the nitritification reaction, also ensures that CO_2 is removed in accordance with reaction equation III. Accordingly, the nitritification reaction has a net yield of one equivalent acid per converted equivalent ammonia. The denitritification reaction according
20 to reaction equation IV requires one equivalent acid per converted equivalent ammonia. This means that by using the CO_2 -stripped effluent from the nitritification reactor, no pH adjustment is required.

By removing CO_2 , the solution subjected to nitriti-
25 fication is stripped of HCO_3^- , lowering the buffering capacity of the solution. This means that its pH may vary, in particular that it may drop due to the formation of acid in this step. The pK of HCO_3^- , that is to say the pH at which HCO_3^- buffers optimally, is 6.37. The drop of the pH
30 inhibits the nitritification process, and ammonia is converted only partly but, according to the understanding provided by the present invention, to the desired extent (namely up to 50%). As a result, a suitable amount of ammonia is available for the subsequent denitritification
35 process which uses acid and thus benefits from the low pH.

Without being bound to any theory, applicant assumes that the good controlling quality is achieved due to the fact that the nitritifying organism only perceives NH_3 and HNO_2 and not NH_4^+ and NO_2^- . When the pH drops the

NH_3 (substrate) concentration decreases and the HNO_2 concentration which inhibits the nitritification reaction, increases.

5 Example

 An agitated batch reactor (2.4 l) was operated without sludge retention and fed with ammonia-rich waste water (41 mM; pH ~ 8.0). During the day 80% of the reactor volume was replenished. The temperature was maintained at
10 33°C and the dissolved oxygen concentration was 20%. Under these conditions the biomass concentration was 140 mg dry weight per litre. The pH of the reactor's effluent was about 6.7. N.B.: the pH was not adjusted by the addition of a substrate compound such as methanol. 40-50% of the
15 ammonia in the waste water was converted.

 1.2 ml/min of the effluent was fed into a fluidized-bed reactor (capacity 2 l). The pH in the fluidized-bed reactor was stable and was about 7.9. Kjeldahl nitrogen was converted in the fluidized-bed reactor
20 at a rate of 0.6 kg N/m³·day. The total removal of nitrogen was 83%. The relevant parameters are given in the Figure.

 This percentage may be increased by returning a portion of the effluent from the fluidized-bed reactor to
25 the batch reactor. Due to the stable pH in the fluidized-bed reactor the amount of return is not very critical and may be set at a permanent value. Too high a return results in an increased degradation of ammonia in the batch reactor. This causes the consumption of acid to drop in the
30 fluidized-bed reactor, as a consequence of which the degradation of ammonia decreases again.

 Although the method according to the invention has a substantially more self-regulatory nature and automatically results in an overall degradation of ammonia of at
35 least about 80%, the pH of the contents of the nitritification reactor may optionally be adjusted by means of the supply of effluent from the denitritification reactor. Thus here no external additive whatsoever is added.

According to another embodiment of the method according to the invention, the waste water is fed to a denitritification step. During denitritification ammonia from the waste stream is used and a portion from the denitritification reactor is fed to the nitritification reactor. There nitrite is formed which is fed to the denitritification reactor.

In the event that the effluent from the denitritification step is discharged, said effluent may first be subjected to a nitrification step in order to avoid nitrite discharge.

Suitable microorganisms may be obtained without great difficulty from sludge of existing water-treatment plants in which ammonia is degraded, in the manner described in the literature. Alternatively, the culture for the denitritification may be obtained from the Centraal Bureau voor Schimmelcultures, Baarn, the Netherlands, registered under number 949.87.

CLAIMS

1. A method of treating ammonia-comprising waste
5 water, wherein in a first step ammonia-comprising waste
water is subjected to a nitrification treatment by using a
nitrifying microorganism and by the addition of oxygen,
yielding a solution comprising an oxidation product of
10 ammonia, and in a second step the oxidation product of
ammonia together with ammonia is converted into nitrogen,
through the influence of a denitrifying microorganism,
characterized in that by using bicarbonate-containing
waste water which is substantially stripped of bicarbonate
by the supply of air, and in the first step maintaining
15 the pH at ≤ 7.2 by controlling the aeration, part of the
ammonia present in the waste water is converted into
nitrite, yielding a nitrite-containing solution, and in
the second step the denitrifying microorganism uses the
thus formed nitrite as oxidant for the remaining ammonia.

20 2. A method according to claim 1, characterized in
that in the first step the ammonia-containing waste water
is fed to a nitritification reactor in an amount such that
the nitritification reactor operates without sludge reten-
tion, the temperature of a solution subjected to nitriti-
25 fication is maintained at between 25 and 60°C and the pH
at between 6 and 7.2.

3. A method according to claim 1 or 2, character-
ized in that in the second step, the temperature of the
solution in the denitritification reactor being subjected
30 to the denitritification treatment is preferably main-
tained at between 25 and 60°C and the pH at between 6 and
9.

4. A method according to claim 1, characterized in
that the first step and the second step are carried out
35 simultaneously in one bioreactor, in which bioreactor
nitrifying and denitrifying microorganisms are present in
a solid phase, the nitrifying microorganism being substan-
tially present in the outer, aerobic part of the solid
phase and the denitrifying microorganism being substan-

tially present in the anaerobic inner part of the solid phase, and oxygen, dependent on the ammonia concentration in the bioreactor, is supplied in an amount limiting the first step.

5 5. A method according to claim 4, characterized in that as solid phase a phase chosen from a biofilm-carrying particulate carrier and a biofilm-carrying immobile carrier is used.

10 6. A method according to claim 1 or 2, characterized in that the temperature of a solution in the reactor being subjected to a denitrification-nitrification treatment is maintained at between 5 and 60°C and the pH at between 6 and 9.

1 / 2

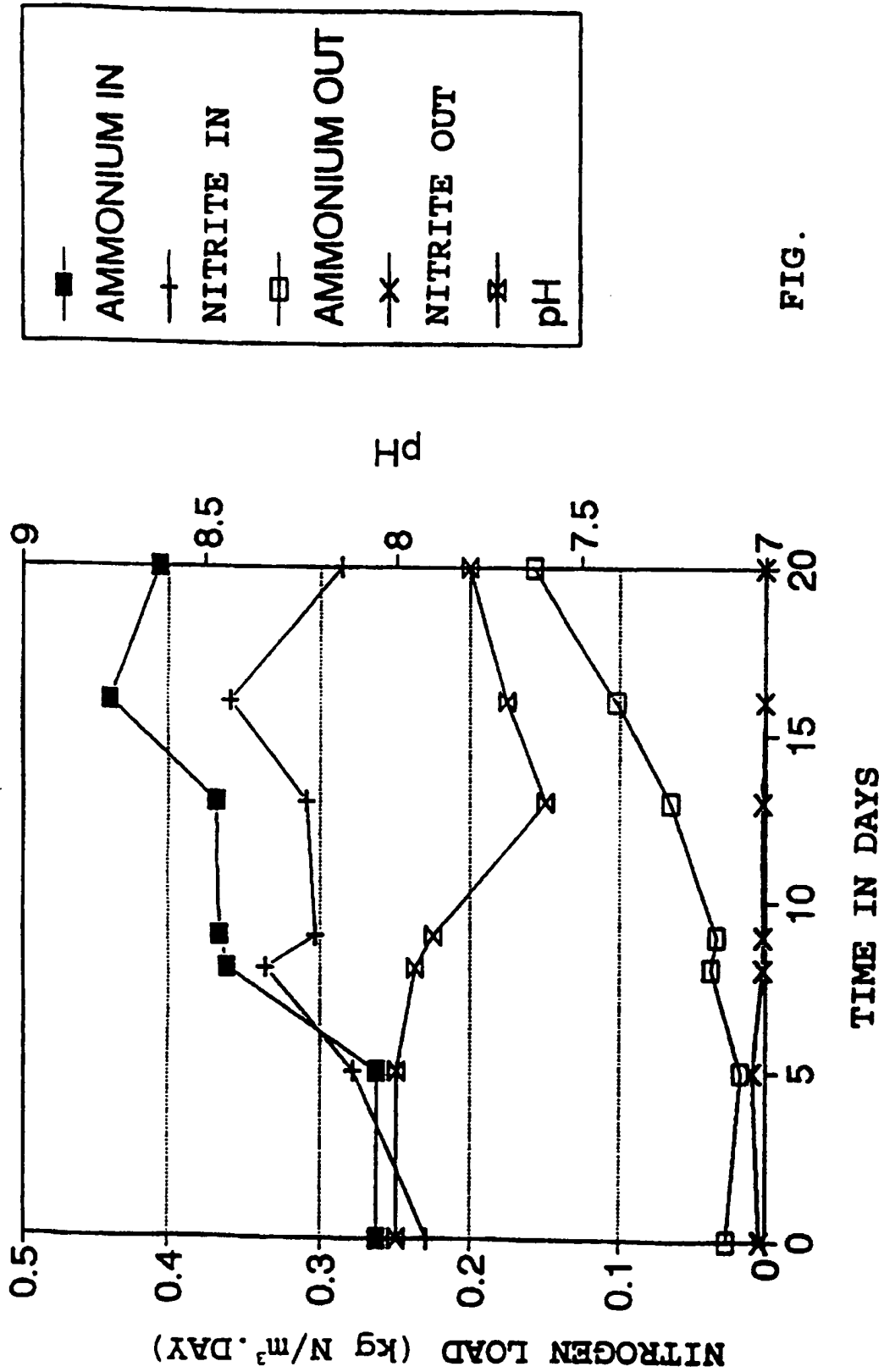
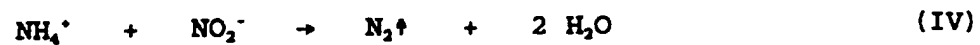
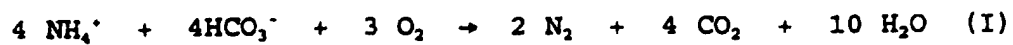


FIG.

2 / 2

FORMULA SHEET

INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 97/00482

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C02F3/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	ARNO SCHRAUWERS: "Eenreactor stistofverwijderingsproces paart eenvoud aan schoonheid" DELFT INTEGRAAL, vol. 12, no. 1, 1995, DELFT-NL, pages 3-7, XP002030429	1-3
A	DE 39 39 732 A (PREUSSAG AG) 6 June 1991	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

17 November 1997

Date of mailing of the international search report

26 11. 97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Kaspers, H

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 97/00482

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 3939732 A	06-06-91	NONE	